

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 21Feb00		3. REPORT TYPE AND DATES COVERED Final 23Apr99-22Jan99
4. TITLE AND SUBTITLE Diode-pumped tunable 3 micron laser sources				5. FUNDING NUMBERS C-DASG60-99 - M -0088
6. AUTHOR(S) Arlete Cassanho, Hans Jenssen				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AC Materials, Inc. 2721 Forsyth Road, Suite 264 Winter Park, FL 32792				8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Army U.S. Army Space and Missile Defense Command P.O. Box 1500 Huntsville, Alabama, 35807-3801				10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distributions unlimited				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) Report developed under SBIR contract for topic number BMDO099-014. The purpose of this work was to evaluate two laser host materials doped with Tm and Dy as potential 3 μ m, diode pumped lasers. BaY ₂ F ₈ single crystals were grown and spectroscopy identified efficient Tm to Dy energy transfer. The Dy stimulated emission cross section was measured to be comparable to other IR lasers. A new crystalline structure, NaYF ₄ was also studied. In this crystal it was found, in addition to efficient pumping, a longer fluorescent lifetime for the 3 μ m Dy laser transition. Both materials are promising candidates for a tunable 3 μ m laser source. Potential benefits: A compact, power scalable frequency agile solid state laser operating near the 3 μ m spectral band is a desired technology for numerous BMDO and DOD programs including various active sensor and countermeasure applications. Commercial applications would be in the area of laser surgery, dentistry and dermatology. Further potential applications would be in instrumentation for scientific and spectroscopic studies, especially the O-H bond.				
14. SUBJECT TERMS 3 micron laser, Dy laser, barium yttrium fluoride laser				15. NUMBER OF PAGES 14
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL	

Standard form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

Ref D

A. INTRODUCTION

A compact, power scalable frequency agile solid state laser operating near the 3 μm spectral band is a desired technology for numerous BMDO and DOD programs including various active sensor and IR countermeasure applications. Ideally, the laser would be pumped directly by diode laser arrays to allow it to operate with maximum efficiency at or near room temperature, and with good beam quality. Preferably, the laser would be compatible with operation in either CW or pulsed mode, which requires level dynamics conducive to high energy storage capability. In recent years, options considered for a laser near 3 μm focused primarily on the erbium (Er^{3+}) ion dopant in various host media, or on down-shifting the frequency of other, shorter wavelength lasers, using an optical parametric conversion process in a nonlinear medium.

Er-doped lasers, which generally emit radiation at specific wavelengths between 2.79 and 2.94 μm (depending on the host crystal) afford, however, tunability in a fairly narrow band - usually less than 100 nm around the line center. This limits wavelength selectivity and may preclude certain applications of choice, for example, where operation within atmospheric propagation windows is desired. Furthermore, lifetime quenching of the upper laser level in erbium-doped lasers pumped by diodes near 950-960 nm present major difficulties for power scaling and render Q-switched operation rather impractical, except for monolithic or guided structures.

The alternative approach using parametric conversion based, for example, on shifting the radiation of an existing 1 μm or 2 μm laser using an optical parametric oscillator (OPO), can provide for tunability across a broad range in the mid-IR but requires a separate pump laser. This limits the overall efficiency of the laser system, even with a diode-pumped fundamental laser, while adding considerable complexity to the overall design. For example, a Nd-doped, 1 μm laser with - at best - 5-10% wall-plug efficiency results in maximum efficiency at the converted 3 micron wavelength of 2-3% at the most, because of the large quantum defect. Alternative pump lasers such as thulium (Tm^{3+}) and holmium (Ho^{3+}) doped crystals which lase, typically, near 2 μm , have been intensively pursued as pump lasers to generate radiation beyond 3 μm , but the parametric conversion process requires use of the more expensive and damage prone chalcopyrite nonlinear crystals such as AgGaSe_2 and ZnSe .

A solid state laser emitting directly at a wavelength longer than 3 μm that would also be tunable over a range spanning more than 200 nm and be more compatible

with diode pumping than erbium-doped lasers is therefore considered to be highly desirable.

In this Phase I SBIR project we proposed to investigate a solid state laser which could potentially meet these requirements. The baseline laser concept was based on a BaY_2F_8 (BYF) crystal co-doped with thulium and dysprosium, whereby the Tm^{3+} ions absorb diode light at or near 800 nm and feed the upper laser level of the active Dy^{3+} ion, through a cross relaxation and an energy transfer process. The Dy ion would then provide the lasing action in the 3 μm region. The hope was that the dynamics of the Tm, Dy system will be analogous to that of the better known, and successfully demonstrated 2 μm Tm, Ho -doped lasers. The specific approach selected for this project grew out of previous efforts by a collaborative work by Jenssen, Cassanho and Toncelli and Tonelli [Ref. 1]. In that work it was demonstrated strong absorption in 10% Tm, 2% Dy doped BYF crystals near 790 nm at room temperature and a broad fluorescence spectrum spanning several lines between 2.85 and 3.4 μm . However, reabsorption losses were also observed in this earlier work, which were considered detrimental for optimal laser performance, especially given the low gains of the subject transitions. As part of the primary goal set for this project we set out to resolve this issue by identifying more optimal compositions of the doped BYF crystal, followed by preliminary laser tests of selected samples.

In addition a new fluoride crystal - NaYF_4 - was investigated and appeared to offer even more promise for operation at the 3 μm range than BYF.

B. PHASE I PROJECT OBJECTIVES.

The primary objective for this project was to evaluate the potential of a barium yttrium fluoride BaY_2F_8 (BYF) crystal co-doped with dysprosium (Dy) and thulium (Tm) as a candidate for producing tunable radiation from 2.8 to 3.4 μm . As part of this objective we aimed to determine feasibility of constructing a diode-pumped laser based on Dy, Tm:BYF. In accordance with this objective, the following goals were set for the project:

1.1 Growth and characterization of Dy, Tm:BYF with varying concentrations for the two dopants. Spectroscopic parameters such as energy transfer and cross-relaxation rates, re-absorption and potential losses due to excited state transitions and gains would be measured to determine optimal dopants concentration.

1.2 Perform laser tests using an end-pumped configuration with a cw Ti:sapphire laser.

1.3 Preliminary lasing test of the best sample crystal using a diode as a pump.

1.4 Compare experimental results to model calculations.

A secondary objective involved the spectroscopic evaluation of NaYF₄, a low-phonon new material. For that we proposed the following goals:

2.1 Growth of NYF boules of varying Dy,Tm concentrations.

2.2 Design of laser cavities and procurement of coated optics

2.3 Determine absorption and emission characteristics of the material as a function of the dopants.

2.4 Attempt to lase the material using a short pulse Ti:sapphire laser as a pump.

2.5 Compare the results to the results obtained with BYF.

C. WORK PERFORMED.

During the course of the Phase I program, we successfully grew two laser quality crystals of Tm,Dy-doped BYF with 10% Tm and 0.4% and 0.2% Dy respectively. We performed spectroscopic measurements to determine upper level lifetimes, emission and energy transfer efficiency of samples fabricated from the crystal boules. We found that the expected cross relaxation in Tm and energy transfer to Dy was an efficient method to excite the Dy ⁶H_{13/2} levels. In both BYF and NYF the Tm ³F₄ lifetime is reduced by at least a factor of 50.

We have also made the first estimate of the Dy 3 μm stimulated emission cross section. Although this is low, it is comparable to that of successful diode pumped Tm laser materials.

The most promising approach involves, however, the new material NaYF. Single crystals of NaYF could not be grown on this Phase I project due to the lack of a dedicated furnace and enough time to develop the crystal growth. The spectroscopic data acquired on polycrystalline samples grown for this project validate the expectation of level dynamics considerably more favorable than BYF. We therefore anticipate that Dy,Tm-doped NaYF will become a gain medium of choice for producing the 3.4 μm radiation and plan to propose this as the baseline for a follow-on Phase II program.

The approach designed to meet the program objectives consisted of five tasks:

1. Dy,Tm:BYF crystal growth and fabrication,
2. Growth of Dy,Tm:NaYF
3. Spectroscopic measurements
4. Preliminary laser tests
5. Analysis, modeling and performance projections.

Task 1. Dy,Tm:BYF crystal growth and fabrication.

In order to avoid losses due to the presence of impurities in the final crystal, starting materials for the crystal growth were prepared at AC Materials from optical grade barium fluoride and high purity yttrium and rare-earth oxides in a hydrofluorinator using electronic grade hydrogen fluoride. The chamber and boat containing the material were made of platinum and platinum/rhodium to avoid introduction of contaminants into the melt. The final, reacted material was crystalline and clear of carbon and it was immediately transferred to a platinum crucible and loaded into a vacuum Czochralski furnace.

The material was heated up slowly in vacuum, so that any moisture present in the chamber would be eliminated without contaminating the charge. After reaching a pressure of about 10^{-6} torr at a temperature around 600 C, high purity argon was introduced into the growth chamber and growth was performed under this inert cover gas.

Based on results from previous growth experiments on BYF crystals, we selected the optimal growth direction "b", or (010) for the seed.

Two crystals were grown, with concentrations of 10 mol% Tm and 0.2 mol% Dy and 10 mol% Tm and 0.4 mol% Dy respectively. They were visually inspected using an intense white light and a He-Ne laser beam and no bubbles, scatter centers or haziness were observed.

The crystals were oriented by Laue x-ray diffraction and sent out for fabrication of spectroscopic samples for evaluation. The spectroscopic samples were oriented in two different directions since BYF is a monoclinic crystal, with laser efficiency dependent on the pump direction. The spectroscopy is reported in Task 3. After

spectroscopic evaluation was performed we had two samples of each boule fabricated as laser elements, with the faces to be pumped oriented as (010) and (100) faces. These samples were then sent out to Quality Thin Films, Oldsmar, Florida for application of coatings in order to reduce losses in the laser system. At the same time, mirrors needed for the laser experiments were made. These coatings are not easy to be applied and only a few companies can do them with reasonable quality. We had the coated laser elements ready only by the end of October and then we started the laser experiments. However, the mirrors were wrong and had to be sent back and re-done. This all delayed the program, but finally we had all that was needed for the diode-pumped laser experiments. These experiments are reported in Task 4.

Task 2. Dy,Tm:NYF crystal growth and fabrication.

We prepared the starting materials for the growth of Dy,Tm:NaYF₄, in the same manner described for the growth of Dy,Tm:BYF. However, the growth of NYF has not been developed yet and we were able to grow only very small crystals, actually, just grains.

Two Dy,Tm:NYF crystals with the same dopant concentrations as for the BYF crystals (10 mol% Tm, 0.2 mol% Dy and 10 mol% Tm, 0.4 mol% Dy), were grown from a very viscous melt of composition 69 mol% NaF and 31 mol% YF₃. This composition was selected based on the phase diagram for the NaF-YF₃ system. For melts richer in YF₃, the crystals go through a destructive phase transition. Due to the nature of the melt, the growth of nucleated grains compete with formation of new grains. If usual procedures for crystal growth are followed, the resulting crystal will have the appearance of tapioca pudding, with intergrowth of NaYF₄ and flux material. The use of diameter control for this kind of crystal is difficult, because the growth rate is slow and changes in temperature driven by deviation of the diameter from its set point will induce formation of new grains. On the other hand, diameter sensing is needed because the sensing device can detect small changes in growth data, not visually observable. When data storage is added to the capabilities, the data can be analyzed after a period of hours and the temperature ramping can be adjusted for another period of time. All this takes a long time and a dedicated crystal growth station. Even though we have been successful in growing single crystal of Pr,Yb-doped NYF in the past, the time allowed for this Phase I project was not enough to develop the growth of singlecrystalline Dy,Tm:NYF. The resulting polycrystal material was single phase however, so that the fluorescence lifetimes measured will be the same for a NYF singlecrystal.

The Dy,Tm:NaYF₄ crystals were pulled from the melt at pulling rates of 0.2 mm/hr. The growth temperature was around 680 C. A platinum crucible was used to contain the melt and the cover gas used was argon.

Task 3. Spectroscopy of Tm,Dy-doped BYF and NYF

Absorption measurements on Tm(10%),Dy(0.4%):BYF were made using a Cary 500 dual beam spectrophotometer with a pair of identical calcite polarizers for obtaining polarization dependent spectra. The results are shown in Figure 1. BYF is a biaxial material and exhibits three distinct absorption spectra, measured in this case along the three principal axes of the refractive index ellipsoid. As the plot indicates, at the peak absorption near 790 nm absorption is strongest for polarization along the y-axis, which is also the material's crystallographic b-axis.

Absorption was not measured in Tm,Dy:NYF as single-crystal samples are not yet available.

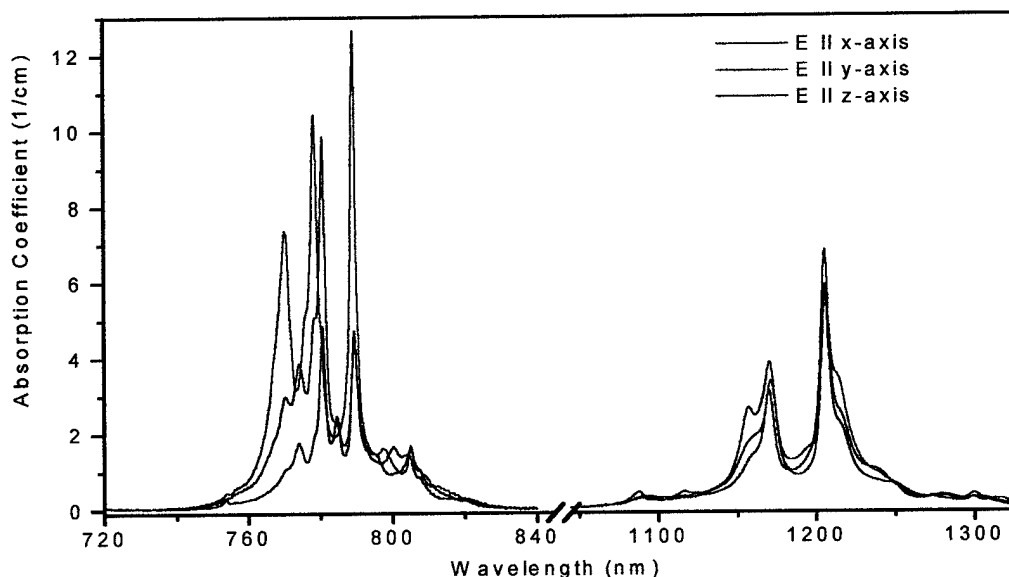


Figure 1. Absorption in Tm(10%),Dy(0.4%):BYF

Emission was measured using a 792 nm fiber-coupled laser diode as the excitation source, a 1/3 meter monochromator with a 300 g/mm grating, and a liquid nitrogen-cooled InSb detector. The results from the Tm(10%),Dy(0.4%):BYF sample are shown in Figure 2. There are four distinct spectra here, since emission polarized along the x-axis (i.e. electric field vector parallel to x-axis) is different

for each of the two possible directions of the magnetic field vector, suggesting the presence of a magnetic dipole contribution to the emission. Emission polarized along the y-axis or z-axis did not exhibit this effect.

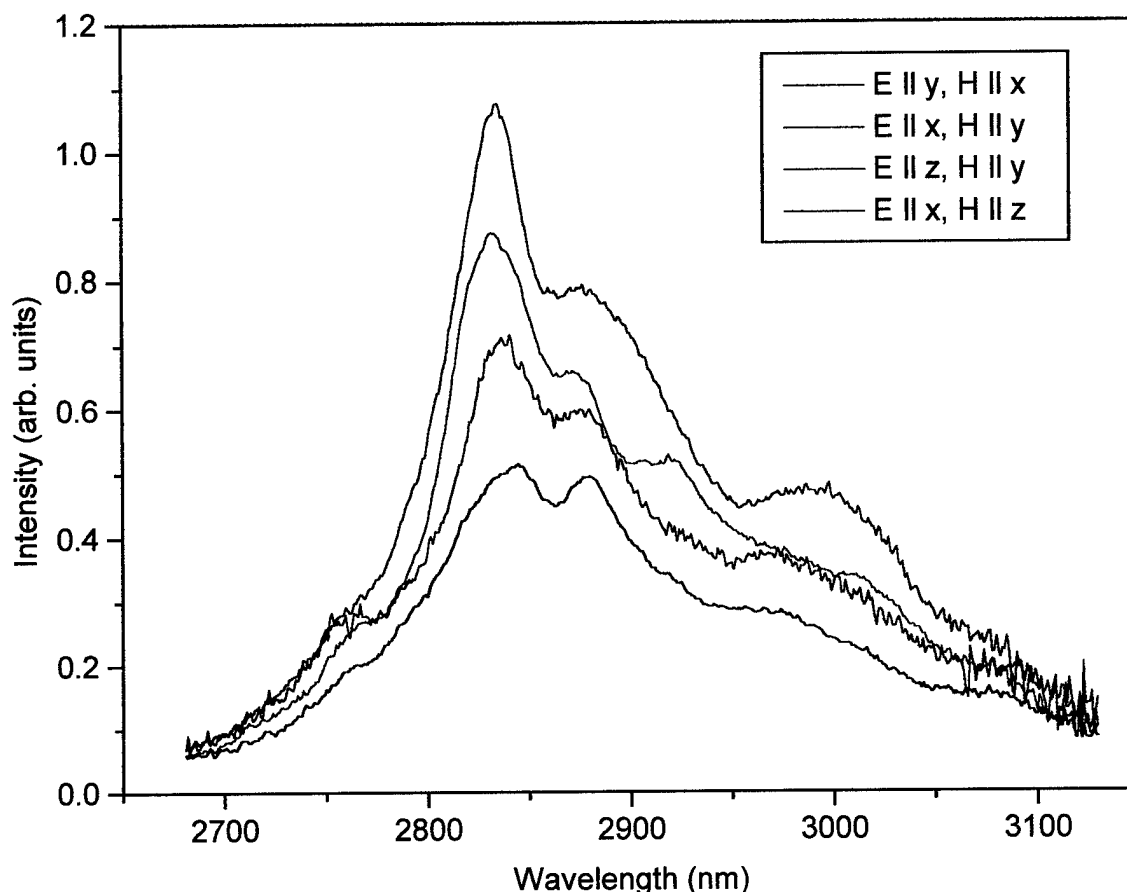


Figure 2. 3 μm emission in Tm(10%),Dy(0.4%):BYF

Figure 3 compares the unpolarized 3 μm emission of the Tm(10%),Dy(0.4%):BYF sample with that of Tm(10%),Dy(0.2%):NYF. Since the Tm,Dy:NYF sample was not an oriented single crystal, meaningful polarized measurements could not be made. As the plot shows, measured emission from the Tm,Dy:NYF sample was over twice that from the Tm,DY:BYF sample. The arbitrary intensity units simply reflect the signal on the detector and do not permit exact quantitative comparison of peak emission, but it can be concluded that emission in the 3 μm region is much stronger with the NYF host material than with BYF, especially considering the higher concentration of Dy in the BYF sample.

Fluorescence lifetime was measured for a variety of Tm,Dy samples using the emission setup described above, with a chopper placed in the pump beam and operated such that the pump fall time was less than 30 μ s. Lifetime was measured for both the 3 μ m Dy emission and 1.9 μ m Tm emission.

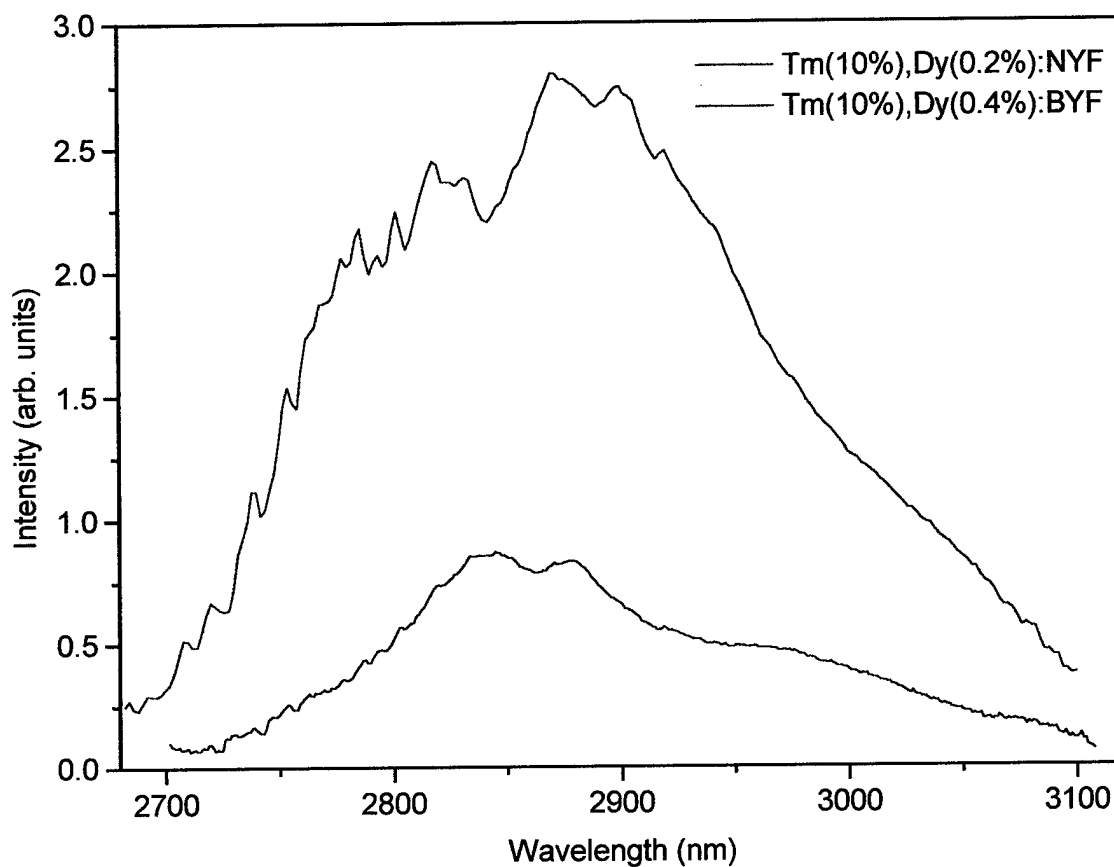


Figure 3. Comparison of 3 μ m emission in Dy,Tm:BYF and Dy,Tm:NYF for the same dopant concentrations

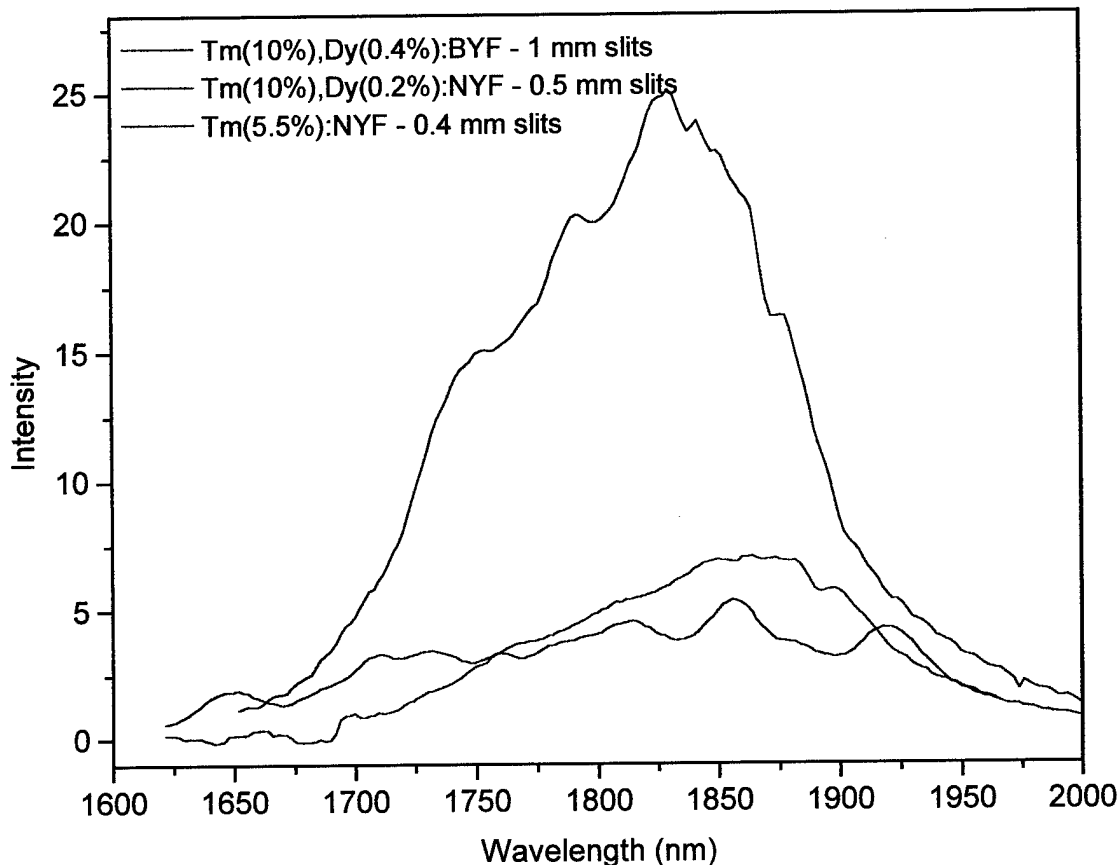


Figure 4. A qualitative comparison between Tm emission at $1.9\ \mu\text{m}$ for singly doped Tm:NYF and BYF/NYF co-doped with Dy.

Table 1 summarizes the results. Lifetime for both transitions is longer in NYF than in BYF, except for the singly Tm-doped samples. Comparison of the results for the two NYF samples reveals that the lifetime of the $1.9\ \mu\text{m}$ transition is affected by Dy concentration, being longer in the sample with a lower Dy concentration where there are fewer Dy ions to accept energy from the Tm. The $3\ \mu\text{m}$ transition lifetime does not share this concentration dependence. In all three codoped samples, the $1.9\ \mu\text{m}$ transition lifetime is much shorter than in the NYF sample doped only with Tm, indicating that the transfer of energy from Tm to Dy is quite efficient for either Dy concentration.

Table I. *Summary of fluorescence lifetime results.*

Material	3 μm Lifetime	1.9 μm Lifetime
Tm(1%):BYF	—	17 ms
Tm(10%),Dy(0.4%):BYF	1.3 ms	110 μs
Tm(10%),Dy(0.4%):NYF	4.5 ms	189 μs
Tm(10%),Dy(0.2%):NYF	4.5 ms	270 μs
Tm(5.5%):NYF	—	10 ms

Task 4. Preliminary laser tests

For the lasing experiment, four samples of Tm,Dy:BYF were prepared, two with 0.4% Dy and two with 0.2% Dy, with different orientations. All the samples had identical dimensions of 7x7 x2.5 mm. The coatings applied were S1: HR at 3400 nm, HT at 789 nm, S2: AR at 3400 nm. The mirrors were 0.5"x0.25"PL/10cmcc CaF₂ with S1: 99%R at 3400 nm and 0.5"x0.25"PL/10 cmcc CaF₂ with S1: 99.5%R at 3400 nm. The 792 nm fiber coupled laser diode used for the spectroscopic measurements served as the pump source. The laser sample was held in a water-cooled mount for heat removal, and a chopper was placed before the collimating optics to reduce average power in the crystal. The experimental arrangement is shown in Figure 5. Up to 750 mW of pump power was delivered to the crystal in a spot with a $1/e^2$ diameter of 450 μm . Lasing, however, was not obtained. In order to increase pump power at the crystal, the doublet lens closest to the crystal was replaced by a single lens with focal length of 25 mm. With this substitution, we pumped the crystal with up to 2 W in a spot with a $1/e^2$ diameter of 640 μm . Lasing, however, was still not achieved, and the sample in use at the time was cracked in two.

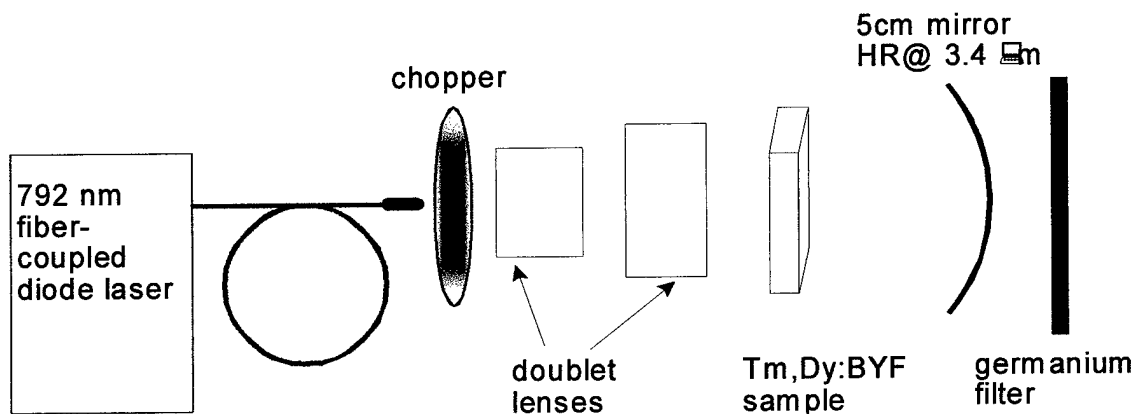


Figure 5. Experimental arrangement for obtaining lasing in Dy,Tm:BYF

A laser diode operating at 792 nm and coupled through a fiber bundle is not at all an ideal pump source for these solid state crystals, and is likely the chief reason why the lasing experiment has so far been unsuccessful. The absorption peak in Tm,Dy:BYF falls at 789.2 nm, and is sufficiently narrow that at least 50 percent of the 792 nm pump is not absorbed. Also, the light out of the fiber bundle cannot be focused to a spot much smaller than that obtained with the original arrangement of two doublet lenses. A Ti:Sapphire laser would be the ideal pump source for this type of experiment since it can be focused to a very small spot, and can be tuned to better match the absorption of the laser crystal. The mirrors we currently have for our Ti:Sapphire laser, however, do not cover the needed spectral region. We have ordered new mirrors and as soon as they are available we will repeat this experiment with the Ti:Sapphire laser as the pump source.

Task 5 Analysis, modeling and performance projections.

Laser action of Dy:BYF at 3 μm has been previously obtained at 77 K and at room temperature in pulsed regime [Ref 2,3]. Our interest is however, to obtain a room-temperature 3 μm laser pumped by a diode-laser. Similarly to the 2 μm Tm:Ho laser, we expect that in Dy:Tm:BYF or Dy,Tm:NYF, Tm will absorb the power from the diode laser and through a cross relaxation and an energy transfer process, feed the upper laser level of the Dy ion generating efficient 3 μm laser emission.

We observed efficient Tm to Dy energy transfer in both BYF and NYF. In BYF, the $\text{Tm}^{3+} {}^3\text{F}_4$ lifetime decreases from 17 ms in only Tm-doped BYF to 110 μs for 0.4% Dy. The Dy ${}^6\text{H}_{13}$ lifetime at room temperature in both samples is 1.3 ms. In NYF, the $\text{Tm}^{3+} {}^3\text{F}_4$ lifetime decreases from 10 ms in only Tm-doped NYF to 270 μs for 0.2% Dy and 189 μs for 0.2% Dy. The Dy ${}^6\text{H}_{13}$ lifetime at room temperature in both samples is 4.5 ms. We obtained a shorter lifetime for the 1.9 μm transition in Tm only doped NYF than in BYF. Since the Tm:NYF sample was not grown in this program, but it was an old sample we had, we cannot rule out any contaminants that can be present. On the other hand, the BYF and NYF crystals grown in this program were made from the same high purity starting materials yttrium, thulium and dysprosium.

In both crystals the energy transfer is therefore quite efficient, greater than 95%, based on the lifetime measurements.

The radiative quantum efficiency of the Dy ${}^6\text{H}_{13}$ multiplet has been estimated for BYF [Ref. 1] and indicates that the radiation lifetime, at room temperature, should be 44 ms. This corresponds to a quantum efficiency of 10%. The resulting stimulated emission cross section for the 3 μm emission ranges from a peak value of $5 \times 10^{-21} \text{ cm}^2$ to $1 \times 10^{-21} \text{ cm}^2$ at 3.4 μm .

For NYF the room temperature fluorescence lifetime is 4.5 ms, however we do not have any estimates of cross sections or radiative quantum efficiencies as yet. Based solely on the lifetime, we expect it to be at least a factor of 3 higher than in BYF (4.5 ms vs. 1.3 ms).

The Dy,Tm:BYF laser measurements were made on 2.5 mm thick samples. Since we had to make a decision on sample size and coatings early in the program, before we had numbers for emission cross-sections, the samples were not optimum for our laser experiments.

When we used the estimated value of the Dy emission cross section, $5 \times 10^{-21} \text{ cm}^2$, we calculated a threshold pump power in our laser experiment of about 5 W. With the thin laser samples (2.5 mm) we would need to invert nearly all the Dy in the laser volume. In addition we did not have the optimum pump source. Future laser experiments should use longer gainlengths, smaller pump beam spot size or side pumping. This latter approach will also yield more efficient heat removal from the laser element.

References:

1. A. Toncelli, M. Tonelli, A. Cassanho, H.P. Jenssen, "Spectroscopy and dynamic measurements of a Tm,Dy:BaY₂F₈ crystal", Journal of Luminescence 82(1999) 291
2. L.F. Johnson, H.J. Guggenheim, Applied Physics Letters 23(1973) 96
3. N. Djeu, V.E. Hartwell, A.A. Kaminskii, A.V. Butashin, Optical Letters 22(1997)997